CHAPTER 8
COAGULANTS, POLYELECTROLYTES, AND COAGULANT AIDS

8-1. Introduction. Numerous chemicals are used in coagulation and flocculation processes. There are advantages and disadvantages associated with each chemical. The designer should consider the following factors in selecting these chemicals:

- Effectiveness.
- Cost.
- Reliability of supply.
- Sludge considerations.
- Compatibility with other treatment processes.
- Environmental effects.
- Labor and equipment requirements for storage, feeding, and handling.

a. A suggested reference for summarizing the above factors is EPA (430/9-79-018), *Chemical Aids Manual for Wastewater Treatment Facilities*. For a more complete bibliography, see Appendix A, *References*.

b. Coagulants and coagulant aids commonly used are generally classified as inorganic coagulants and polyelectrolytes. Polyelectrolytes are further classified as either synthetic-organic polymers or natural-organic polymers.

8-2. Inorganic Coagulants. The three main classifications of inorganic coagulants are:

- Aluminum derivatives.
- Iron derivatives.
- Lime.

With exception of sodium aluminate, all common iron and aluminum coagulants are acid salts and, therefore, their addition lowers the pH of the treated water. Depending on the influent's pH and alkalinity (presence of $HC0_{3-}$, $C0_3^{2-}$, and OH^-), an alkali, such as lime or caustic, may be required to counteract the pH depression of the coagulant. This is important because pH affects both particle surface charge and floc precipitation during coagulation. The optimum pH levels for forming aluminum and iron hydroxide flocs are those that minimize the hydroxide solubility (EPA, 1987). However, the optimum pH for coagulating suspended solids does not always coincide with the optimum pH for minimum hydroxide floc solubility. Table 8-1 lists several common inorganic coagulants along with associated advantages and disadvantages.

Table 8-1
Advantages and Disadvantages of Alternative Inorganic Coagulants

Name	*Advantages*	*Disadvantages*
Aluminum Sulfate (Alum) $Al2(SO_4)_3.18H_2O$	Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to water; effective over a limited pH range.
Sodium Aluminate $Na_2Al_2O_4$	Effective in hard waters; small dosages usually needed	Often used with alum; high cost; ineffective in soft waters
Polyaluminum Chloride (PAC) $Al_{13}(OH)_{20}(SO_4)_2.Cl_{15}$	In some applications, floc formed is more dense and faster settling than alum	Not commonly used; little full scale data compared to other aluminum derivatives
Ferric Sulfate $Fe_2(SO_4)_3$	Effective between pH 4–6 and 8.8–9.2	Adds dissolved solids (salts) to water; usually need to add alkalinity
Ferric Chloride $FeCl_3.6H_2O$	Effective between pH 4 and 11	Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum
Ferrous Sulfate (Copperas) $FeSO_4.7H_2O$	Not as pH sensitive as lime	Adds dissolved solids (salts) to water; usually need to add alkalinity
Lime $Ca(OH)_2$	Commonly used; very effective; may not add salts to effluent	Very pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality

a. Aluminum Derivatives. Common aluminum coagulants include aluminum sulfate (alum), sodium aluminate, and polyaluminum chloride. Dry alum is available in several grades, with a minimum aluminum content (expressed as %$A1_20_3$) of 17%. Liquid alum is about 49% solution, or approximately 8.3% by weight aluminum as $A1_20_3$. Alum coagulation works best for a pH range of 5.5 to 8.0; however, actual removal efficiency depends on competing ions and chelating agent concentrations.

(1) Sodium aluminate is an alternative to alum and is available in either dry or liquid forms, containing an excess of base. Sodium aluminate provides a strong alkaline source of water-soluble aluminum, which is useful when adding sulfate ions is undesirable. It is sometimes used in conjunction with alum for controlling pH.

(2) Polyaluminum chloride (PAC), another aluminum derivative, is a partially hydrolyzed aluminum chloride solution. Although still not widely used, it has been reported to provide stronger, faster settling flocs than alum in some applications.

b. Iron Derivatives. Iron coagulants include ferric sulfate, ferric chloride, and ferrous sulfate (copperas). Compared to aluminum derivatives, iron coagulants can be used successfully over a much broader pH range of 5.0 to 11.0. However, when ferrous compounds are used, the solution is typically chlorinated before it is sent into the coagulation vessel. As this reaction produces both ferric chloride and ferric sulfate, chlorinated ferrous sulfate has the same field of usefulness as the other iron coagulants. Because ferrous sulfate works better in feeding devices, compared with the ferric coagulants, chlorinated copperas is sometimes preferred. The ferric hydroxide floc is heavier than alum floc and therefore settles more rapidly.

c. Lime. Although lime is primarily used for pH control or chemical precipitation, it is also commonly used as a co-coagulant.

8-3. Polyelectrolytes. Polyelectrolytes are water-soluble organic polymers that are used as both primary coagulants and coagulant aids. Polyelectrolytes are generally classified as follows:

- Anionic—ionize in solution to form negative sites along the polymer molecule.
- Cationic—ionize to form positive sites.
- Non-ionic—very slight ionization.

Polyelectrolyte primary coagulants are cationic, containing materials with relatively low-molecular weights (generally less than 500,000). Cationic charge density (available positive-charged sites) is very high.

a. Coagulant aids, which are polyelectrolytes, may be anionic, cationic, or near-neutrally charged. Their molecular weights are relatively high (range up to 20,000,000). They function primarily through interparticle bridging.

b. The efficiencies of polyelectrolyte primary coagulants depend greatly on the exact nature of the turbidity particles to be coagulated, the amount of turbidity present, and the turbulence (mixing) available during coagulation.

8-4. Polyelectrolytes vs. Inorganic Coagulants. Although they cannot be used exclusively, polyelectrolytes do possess several advantages over inorganic coagulants. These are as follows.

- During clarification, the volume of sludge produced can be reduced by 50 to 90%.
- The resulting sludge is more easily dewatered and contains less water.

- Polymeric coagulants do not affect pH. Therefore, the need for an alkaline chemical such as lime, caustic, or soda ash is reduced or eliminated.
- Polymeric coagulants do not add to the total dissolved solids concentration.
- Soluble iron or aluminum carryover in the clarifier effluent can result from inorganic coagulant use. By using polymeric coagulants, this problem can be reduced or eliminated.

8-5. Coagulant Aids. The coagulation process is often enhanced through the use of coagulant aids (or flocculants). Sometimes, excess primary coagulant is added to promote large floc sizes and rapid settling rates. However, in some waters, even large doses of primary coagulant will not produce a satisfactory floc. In these cases, a polymeric coagulant aid can be added after the coagulant, to hasten reactions, to produce a denser floc, and thereby reducing the amount of primary coagulant required. Because of polymer "bridging," small floc particles agglomerate rapidly into larger more cohesive floc, which settles rapidly. Coagulant aids also help to create satisfactory coagulation over a broader pH range. Generally, the most effective types of coagulant aids are slightly anionic polyacrylamides with very high-molecular weights. In some clarification systems, non-ionic or cationic types have proven effective. The two types of coagulant aids discussed below are synthetic-organic and natural-organic.

a. *Synthetic Organic Coagulant/Coagulant Aids*. Synthetic organic polymers are the most commonly used coagulant aids for coagulation/flocculation of heavy metal precipitates (EPA, 1987). This is because metallic precipitates typically possess a slight electrostatic positive charge resulting from charge density separation. The negatively charged reaction sites on the anionic polyelectrolyte attract and adsorb the slightly positive charged precipitate (EPA, 1987). Synthetic organic polyelectrolytes are commercially marketed in the form of dry powder, granules, beads, aqueous solutions, aqueous gels, and oil-in-water emulsions (EPA, 1987). Generally, liquid systems are preferred because they require less floor space, reduce labor requirements, and reduce the potential for side reactions because the concentrate can be diluted in the automatic dispensing systems (EPA, 1987). Typical dosage requirements for metals-containing waters are in the 0.5- to 2.0-mg/L range. Polyelectrolytes work most effectively at alkaline and intermediate pHs but lose effectiveness at pH levels lower than 4.5 (EPA, 1987).

b. *Natural Organic Coagulant Aids*. Coagulant aids derived from natural products include starch, starch derivatives, proteins, and tannins (EPA, 1987). Of these, starch is the most widely used. The price per kilogram for these natural products tends to be low; however, dosage requirements tend to be high (EPA, 1987). In addition, because of the composition of natural products, they are more susceptible to microbiological attack, which can create storage problems.